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## SPECIFICS OF SILICON NITRATION

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The sequence of formation of silicon nitride phases inside the volume of an initial silicon grain heated in a gaseous nitrogen medium is studied. Technologies for making ceramics articles based on silicon nitride are proposed.

The heterogeneous reaction of nitrogen with silicon is one of the methods for producing silicon nitride.

**Nitration of silicon powder.** The initial material was silicon KR-O with a specific surface area of 5.5 m<sup>2</sup>/g. The powder was placed in corundum crucibles of diameter 50 mm, and the powder column height was 50 mm. Nitration was implemented in a nitrogen medium within a temperature interval of 1100 – 1300°C. Temperature was measured using thermocouples W/Re-20/5 in the furnace volume, near the surface of the powder, and in the center of the powder volume.

The temperature growth rate in the powder volume significantly exceeded the temperature growth rate inside the furnace in the entire temperature interval considered since reaching 1100°C (Fig. 1). The maximum temperature in the powder volume is reached 3 – 5 min after a difference in the heating rates of the powder and the furnace is registered. The maximum difference between the powder and the furnace temperatures registered at the furnace temperature of 1100 – 1200°C was constant and equal to 90°C. As the furnace temperature increases, the maximum difference in temperatures grows and reaches 160°C at 1300°C, i.e., the powder temperature exceeds the silicon melting point equal to 1410°C. As the heating duration grows, the powder temperature smoothly decreases to the furnace temperature.

In the material obtained at the furnace temperature of 1250°C residual silicon is uniformly distributed over the whole volume. The phase composition of silicon nitride has a constant volume as well,  $\alpha$ -silicon nitride prevailing, although with increasing furnace temperature the quantity of  $\beta$ -phase monotonically grows. Thus, at 1100°C the  $\beta : \alpha$  ratio is equal to 0.05 and at 1200°C it is equal to 0.20. Starting with a furnace temperature of 1250°C, the phase composition of silicon nitride in the center and at the periphery becomes different: the content of  $\beta$ -silicon nitride in the center is higher than at the periphery ( $\beta : \alpha$  is 0.25 and 0.22, respec-

tively). At 1300°C this difference becomes even more perceptible:  $\beta : \alpha$  is equal to 0.40 and 0.27, respectively. Moreover, at the furnace temperature of 1300°C a visible difference between the zones of material is registered: elemental silicon is virtually absent in the central part and the peripheral zone is rich in silicon. Part of silicon is represented by spheroid formations of diameter 30 – 60  $\mu$ m coated by a loose layer of finely disperse silicon nitride.

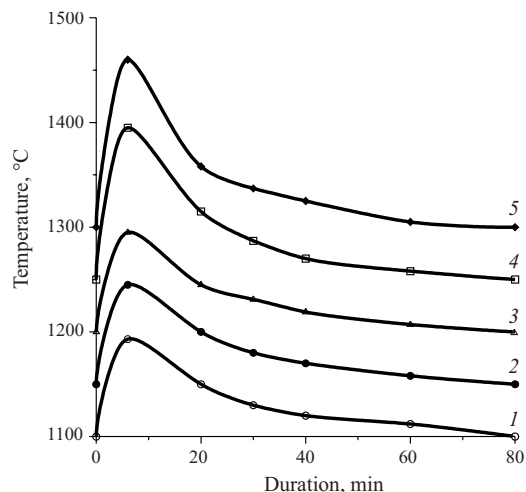
The dependence of the degree of transformation of silicon into silicon nitride depending on nitration duration is shown in Fig. 2. The temperature inside the furnace was kept equal to 1250°C, since this is the maximum temperature below which no zonal distinctions related to the distribution of elemental silicon are registered. Virtually complete transformation of silicon into silicon nitride is reached in 24 h (Fig. 2, curves 1 and 2). The phase composition of emerging silicon nitride does not remain constant with time: the ratio of  $\beta : \alpha$  phases decreases from 0.4 after 3 h to 0.1 after 24 h.

The differences in the phase composition of silicon nitride and emergence of zonal structuring in the material are due to the thermal effect of the reaction between nitrogen and silicon.

It is known that the reaction of silicon with nitrogen is an exothermic reaction with a thermal effect of 750 kJ/mole [1]. This is responsible for the increased temperature inside the powder volume, which indicates the start of perceptible interaction between silicon and nitrogen. As the furnace temperature increases, the rate of formation of silicon nitride grows and, accordingly, the rate of heat release increases. The conditions of heat exchange between the powder and the furnace volumes deteriorate; consequently, the powder temperature becomes even higher. At the furnace temperature of 1300°C the powder temperature reaches 1460°C, i.e., exceeds the silicon melting point.

Temperature variations inside the powder volume determine the specifics of the structure and phase composition of material obtained. With a furnace temperature below 1250°C,

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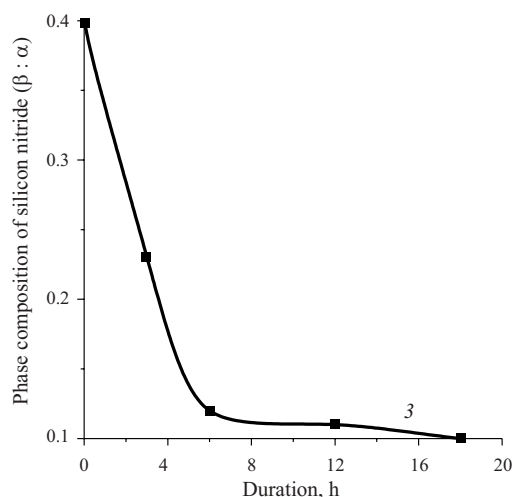
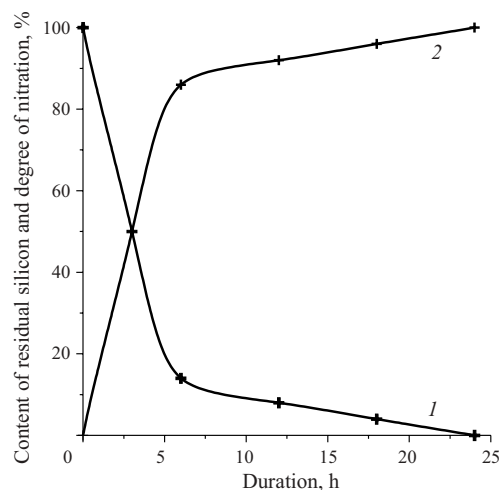
**Fig. 1.** Temperature variations in powder volume versus heating duration for the furnace temperature of 1100°C (1), 1150°C (2), 1200°C (3), 1250°C (4), and 1300°C (5).

the temperature in the powder volume is not higher than 1300°C and the emerging material has a homogeneous composition of silicon nitride in the center and at the periphery. With a furnace temperature of 1300°C, the temperature in the powder volume reaches 1460°C, which leads to local melting of elemental silicon particles. As a result, liquid silicon drops appear and merge. The increase in the size of silicon drops reduces the surface area of the heterogeneous reaction of silicon with nitrogen and decreases the quantity of emerging silicon nitride. For this reason the quantity of heat release decreases, the temperatures in the furnace and in the powder volume become equal and, consequently, the silicon melt crystallizes. However, before crystallizing, melted silicon migrates from the central area of the material to the periphery, which is responsible for the absence of elemental non-reacting silicon in the central zone, which is unusual for a heterogeneous gas – solid reaction, and its presence in the peripheral part.

The increase in the temperature in the volume of powder observed at 1300°C is accompanied by an increased content of  $\beta$ -silicon nitride in the center. The growth of temperature presumably stimulates the polymorphic transformation  $\alpha \rightarrow \beta$  in silicon nitride.

At the furnace temperature of 1250°C the increase in the powder temperature in the beginning of nitration leads to more intense formation of  $\beta$ -silicon nitride by means of a polymorphic transformation; whereas subsequent decrease in the powder temperature delays the polymorphic transformation and silicon nitride is present in the form of the  $\alpha$ -modification.

It is desirable to perform nitration of silicon in conditions ensuring the highest possible content of the  $\alpha$ -phase of silicon nitride. Therefore, the effect of additives on nitration of silicon was investigated. The additive selected was  $V_2O_5$  introduced into silicon powder by various methods. This

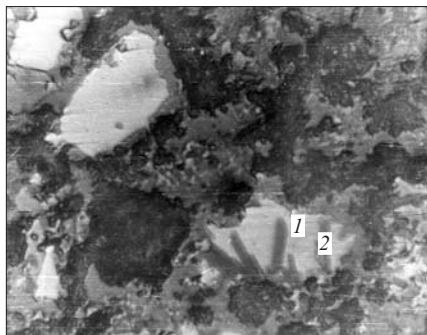


**Fig. 2.** Quantity of residual silicon (1), degree of nitration (2), and phase composition of silicon nitride (3) versus nitration duration at the furnace temperature of 1250°C.

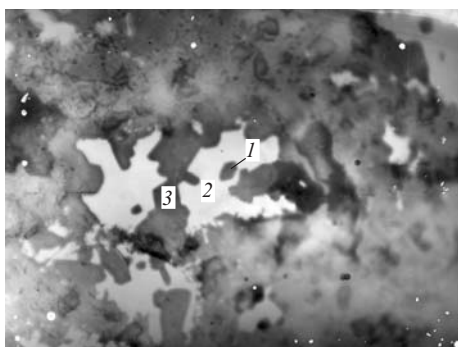
choice of yttrium oxide was due to the fact that it is often introduced in silicon nitride powder as a sintering additive [2].

The results of nitration in this case are somewhat different. With a mass content of yttrium oxide equal to 5%, residual silicon is absent already after 2.5 h at the nitration temperature of 1300°C. At the same time, there is no melting of silicon registered and no differences in the phase composition across the volume of material. Furthermore, as the rate of the temperature rise increases, the ratio between the phases  $\beta : \alpha$  decreases perceptibly, being equal to 1.7 at 400 K/h and 0.06 at 2600 K/h. In addition to  $\alpha$ - and  $\beta$ -phases of silicon nitride, the material obtained contains a phase with the composition  $10Y_2O_3 \cdot 9SiO_2 \cdot Si_3N_4$ .

Thus, the phase composition of silicon nitride produced by nitration of silicon powder depends on the process temperatures, nitration duration, and the effect of specially introduced additives. The exothermic effect of interaction between silicon and nitrogen can be the reason for melting of



**Fig. 3.** Directed formation of crystals of the new phase ( $\times 380$ ): 1) residual silicon; 2) hexagonal prisms (section parallel to the axis).



**Fig. 4.** Silicon grain split by intergrown crystals of the new phase ( $\times 380$ ): 1) hexagonal prism (section perpendicular to the axis); 2) residual silicon; 3) intergrown crystals of the new phase.

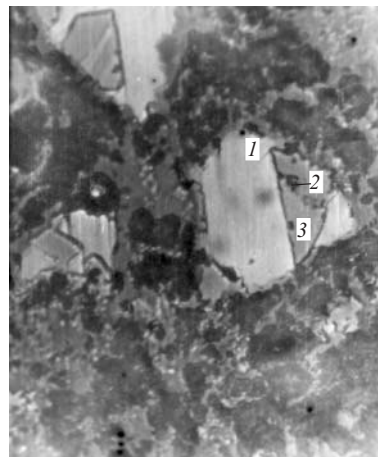
silicon that has not yet reacted, its concentration in the peripheral zone of material, and heterogeneity of the phase composition of silicon nitride.

**Nitration of articles molded from silicon powder.** Nitration of molded silicon articles is of practical interest, since this process produces ceramics made of reaction-sintered silicon nitride.

The formation of a new phase, namely silicon nitride, and of the ceramic microstructure was investigated on samples containing silicon grains sized 60–80  $\mu\text{m}$ . This grain size was chosen since it is sufficiently fine to ensure an intense heterogeneous reaction between silicon and nitrogen, and at the same time sufficiently coarse to allow for optical microscope observation of the formation of the new phase across the section of a silicon grain.

Molded articles were subjected to nitriding firing at temperature of 1250, 1350, and 1450°C and then polished sections were obtained from nitrated samples for microscopic analysis.

The quantity of the new phase in samples fired at the temperature of 1250°C is equal to 25–30% and it is distributed nonuniformly across the sample section. The content of the new formation in the surface zone is significantly higher than in depth. The reaction between nitrogen and sili-



**Fig. 5.** Presence of a second phase in the volume of emerging crystals ( $\times 380$ ): 1) residual silicon; 2) finely crystalline phase; 3) crystal of the new phase.

con in these conditions proceeds only on the surface of the grains, and the emerging silicon nitride covers the entire surface with a dense layer, so that boundaries of coalescence of seeds and possibly crystals of the new phase are not visible on the grain surface.

Samples fired at 1350°C still contain 35–40% non-reacting free silicon. Some silicon grains exhibit a characteristic texture formed due to directed growth of the new formation into the depth of the silicon grain. This is externally manifested in the fact that idiomorphic crystals are formed inside the silicon grain in the form of hexagonal pore-free prisms, their long axis directed toward the silicon grain center (Fig. 3). The cross-section of the prisms reaches 8–10  $\mu\text{m}$ . Prisms growing toward each other meet and agglomerate without leaving a visible trace on the site of their interaction. The silicon grain in this case becomes split (Fig. 4).

The pore-free new phase does not remain constant during its formation. Regardless of the temperature and duration of nitration, a second phase starts crystallizing in the volume of the dense new formation (Fig. 5), whose crystals have sizes of a fraction of a micron. This phase in immersion specimens represents isolated clusters of fine isometric crystals not bonded to each other.

The samples fired at 1450°C differ from those described above by a more intense course of all processes. However, these samples typically have more pores, the pores emerging mainly at the site of formation of the fine-crystalline second phase (Fig. 6a). This may be attributed to crumbling due to very weak adhesion of the fine-crystal formations to each other and to adjacent newly formed grains. With an increasing storage period, the exterior of polished sections changes even more, including certain large grains falling out (Fig. 6b), which can be attributed as well to weak bonds between crystals in the newly formed phase. Crumbling of the fine crystalline phase takes place even in sections impregnated with Canadian balsam, which is evidence of the ab-

sence of the impregnating liquid in this phase. Consequently, the fine crystalline phase is formed inside a matrix crystal.

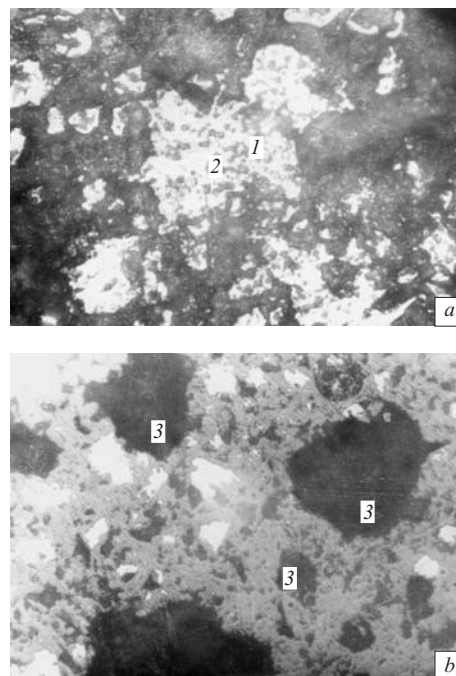
The phase composition of materials can be inferred from the x-ray diffraction data, which indicate the prevalence of  $\alpha$ -silicon nitride in samples nitrated at 1350°C ( $\beta : \alpha = 0.42$ ) and  $\beta$ -silicon nitride in samples nitrated at 1450°C ( $\beta : \alpha = 2.14$ ). It can be assumed that the emerging pore-free phase is  $\alpha$ -silicon nitride and the phase emerging in the course of subsequent heat treatment is  $\beta$ -silicon nitride.

The process of formation of silicon nitride in the heating of elemental silicon in a nitrogen medium can be represented as follows. At the initial stage a silicon grain is coated over its entire surface with a dense layer of silicon nitride, and the reaction is intense enough already at 1250°C. At subsequent stages of the reaction, crystals with extended facet ( $\bar{1}2\bar{1}0$ ) grow on dense silicon nitride formations as on a substrate. This suggests that the initial layer of dense silicon nitride is formed by crystals with extended facet (0001). Consequently, conditions are formed, in which the axis  $C$  of emerging silicon nitride nuclei is directed normally to the surface of the silicon grain. In this case facets ( $\bar{1}2\bar{1}0$ ) of silicon nitride crystals grow more intensely.

Since active growth of facets ( $\bar{1}2\bar{1}0$ ) is due to the chemical retraction of nitrogen with silicon occurring on them, it can be assumed that the coefficient of atom or ion diffusion on this facet is significantly higher than on facet (0001) and even more so than in the volume of the crystal; consequently, coalescence becomes possible precisely for the facets that experience intense growth. Therefore, a layer of dense silicon nitride is formed on the grain surface. However, considering that nuclei of silicon nitride crystals have a symmetry of axis of the sixth order, it is highly probably that growing neighboring crystals are highly disoriented with respect to each other and, accordingly, not all neighboring facets coalesce; therefore, an interface emerges between the crystals. It is evident that the process of nucleation of silicon nitride crystals depends on the state of the surface of the initial silicon grains, consequently, nucleation, orientation, and concentration of silicon nitride crystals can be controlled by modifying the grain surface.

The chemical reaction of nitrogen with silicon does not stop at the next stage of the process after the formation of the silicon nitride layer over the whole surface of the silicon grain, which is evidenced by the fact that the content of silicon nitride keeps growing with an increasing process duration. Consequently, nitrogen continues arriving at the reaction zone, presumably along the interfaces of silicon nitride crystals, which have come close but have not coalesced due to their different orientation.

A silicon grain is rarely homogeneous and free of defects. Therefore, there are sites of predominant occurrence of the reaction between nitrogen and silicon. This is facilitated by a local temperature increase due to the exothermic reaction of nitrogen with silicon. The temperature increase accelerates the reaction at a particular point and, furthermore, lo-



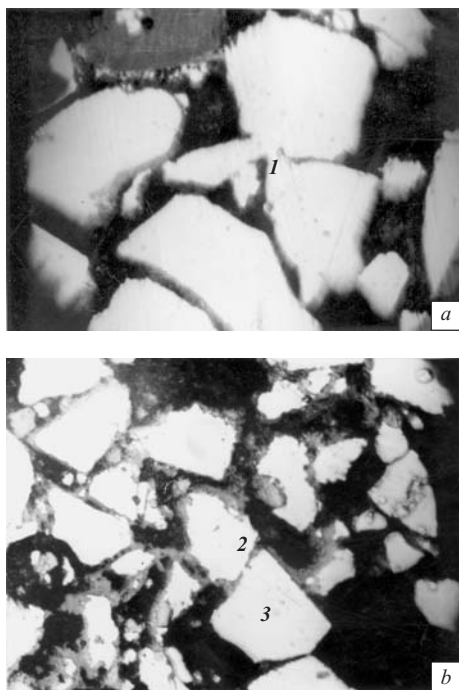
**Fig. 6.** Polished section (*a*) and structure (*b*) of ceramics after prolonged storage ( $\times 380$ ): 1) new phase crystal; 2) pore on the site of fine crystalline phase; 3) pore on the site of initial silicon grains.

cal melting of silicon becomes possible, which also facilitates the heterogeneous reaction. Accordingly, there are areas of predominant formation of silicon nitride in the form of idiomorphic crystals, and conditions for intense growth of crystal facet (0001) exist at this stage, i.e., the silicon nitride crystal is growing into the silicon grain.

The fronts of the growing silicon nitride crystals may meet and, since the chemical reaction proceeds precisely on these fronts, they may coalesce. This results in splitting the initial silicon grain. As nitration of the grain continues, simultaneously with the formation of  $\alpha$ -silicon nitride,  $\beta$ -silicon nitride is formed in the grain volume due to the  $\alpha \rightarrow \beta$  transformation. This transformation is random, and the adjacent crystals of the  $\beta$ -phase are formed regardless of each other and do not coalesce either with each other or with the matrix crystal of the  $\alpha$ -phase. The polymorphic transformation obviously does not contribute to strengthening of the ceramic material formed, despite the absence of perceptible volume variations during the  $\alpha \rightarrow \beta$  transformation. Integrity and strength of ceramics depends not only on the volumetric effects but also on the mechanism of polymorphic transformations.

To make the whole sample strong, it is necessary to create conditions facilitating coalescence of the facets of silicon nitride crystals located on adjacent silicon grains. One of such factors is the need for preliminary coalescence of initial silicon grains under thermal treatment, even before the start of an intense reaction of nitrogen with silicon. It was virtu-



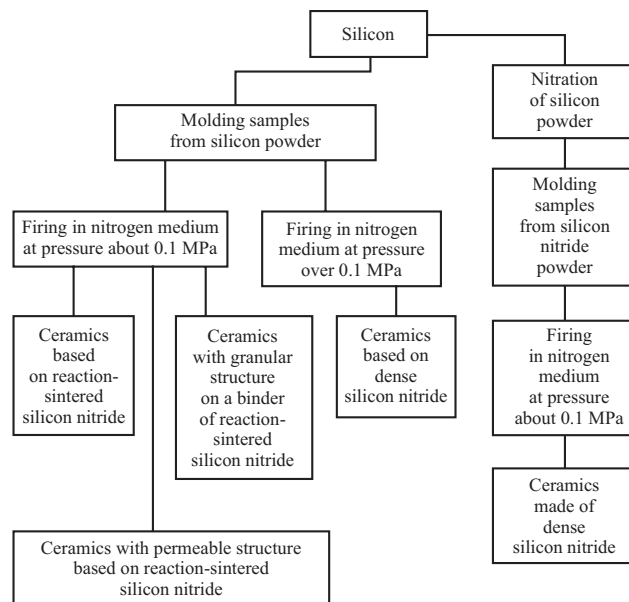


**Fig. 7.** Coalescence of silicon grains (*a*) and structure of nitrated silicon molded sample (*b*) after pretreatment in a helium medium ( $\times 380$ ): 1) site of coalescence of three silicon grains; 2) silicon nitride belonging to adjacent silicon grains; 3) residual silicon.

ally impossible to detect coalescence of crystals of silicon nitride emerging on adjacent silicon grains in the structure of samples containing silicon grains sized 60–80  $\mu\text{m}$  and heat-treated in a nitrogen medium at 1350°C. To ensure such coalescence, a molded silicon sample was preliminary treated in a helium medium at a temperature of 1300°C. Silicon grains in this case become sintered to each other (Fig. 7*a*). Nitration of such structure makes it possible to obtain silicon nitride crystals belonging to adjacent silicon grains in the volume of the sample (Fig. 7*b*).

Since silicon powder used for making ceramics based on reaction-sintered silicon nitride has a high degree of dispersion, the probability of a direct contact between silicon grains is high, and adjacent silicon grains presumably have time to coalesce at the heat treatment stage prior to the reaction between nitrogen and silicon. This, in turn, largely determines the formation of an extended matrix of silicon nitride, which results in substantial mechanical strength of reaction-sintered silicon nitride.

The increased packing density of initial silicon grains facilitates their sintering to each other. However it is essential not only to ensure packing density of silicon grains, but also to develop good contacts between silicon particles in the total volume of the article. This is necessary since silicon has poor sinterability, and shrinkage of articles molded from silicon powder at 1350°C does not exceed 0.4%.



**Fig. 8.** Technological scheme of production of silicon nitride materials.

Thus, the two prerequisites for producing strong ceramics based on silicon nitride are the following:

- using molding methods in preparing articles from silicon powder not only to produce the required shape but also to ensure formation of extended contacts between neighboring silicon particles;
- producing ceramics under conditions in which silicon nitride is formed in the  $\alpha$ -modification.

Satisfying the above prerequisites makes it possible to offer a technology for making following ceramic products based on silicon nitride (Fig. 8):

- articles of different shapes based on reaction-sintered silicon nitride with bending strength about 210 MPa and porosity 25%;
- articles with a granular structure based on a binder from reaction-sintered silicon nitride; in this case the granular filler can be chosen from such available and inexpensive materials as chamotte, corundum, and other oxides, without impairing the properties of the material;
- permeable articles with gas permeability coefficient of 25–2500  $\mu\text{m}^2$  and water permeability up to 300  $\mu\text{m}^2$ ;
- articles of different shapes based on silicon nitride sintered in a nitrogen medium under a pressure of 0.1–20.0 MPa with bending strength up to 800 MPa and porosity 0–3%.

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